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(54) Abstract Title
Analysing liquid samples

(57) A liquid sample is analysed for an analyte using apparatus comprising a vessel e.g. of pliable plastics,with a main sample chamber 101 containing test liquid 109 and an analysing region 102 having an openable/closeable aperture 106 for insertion of a sensor. A liquid flow path 104 connects the chamber 101 and the analysing region 102. At least some of the sample is transferred, e.g. by squeezing the vessel, for analysis via the path 104. Also claimed is (a) apparatus with a sensor support mounted over the aperture 106 (b) a support component for the sensor (c) apparatus characterised by a baffle arrangement and (d) apparatus with an electrochemical sensor and a sensor mounting.

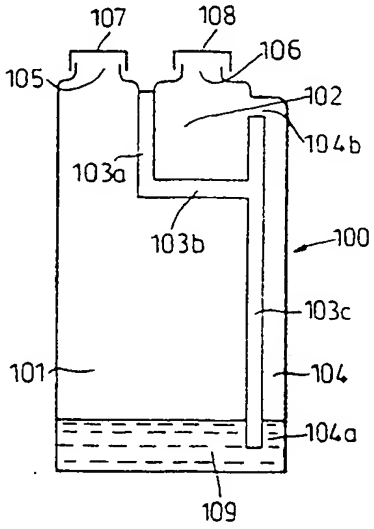

Fig. 1

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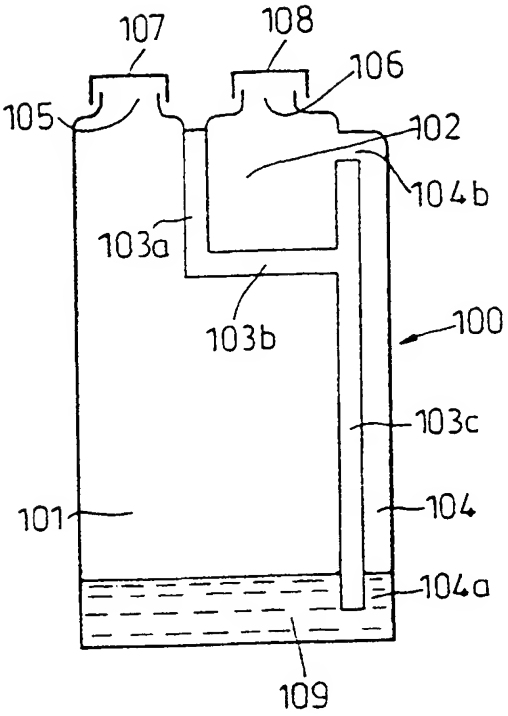

Fig. 1

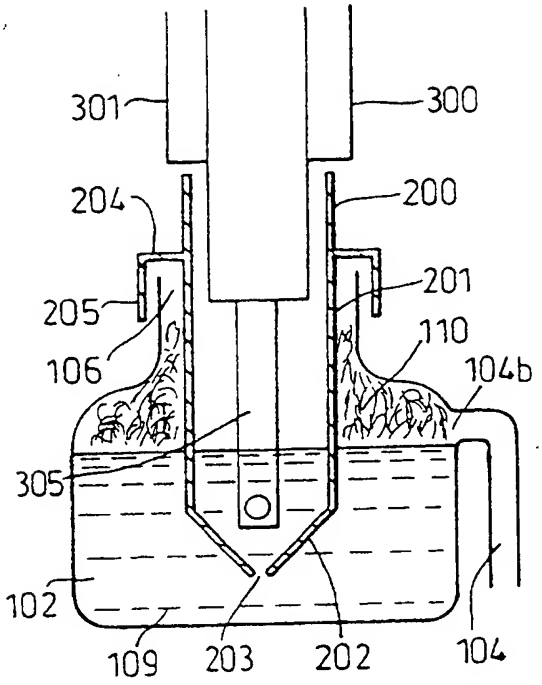

Fig. 2

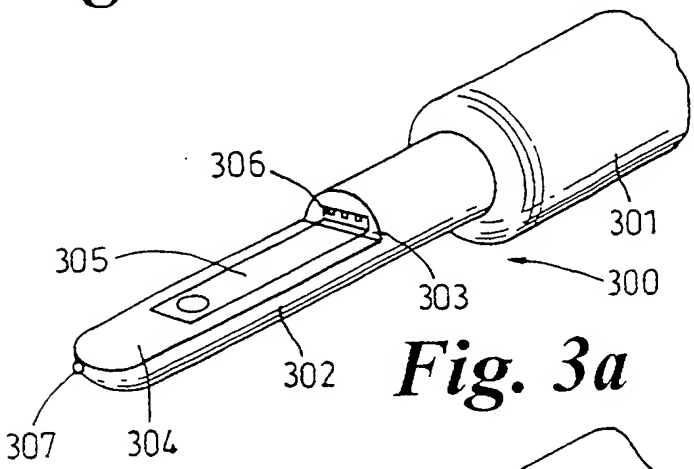

Fig. 3a

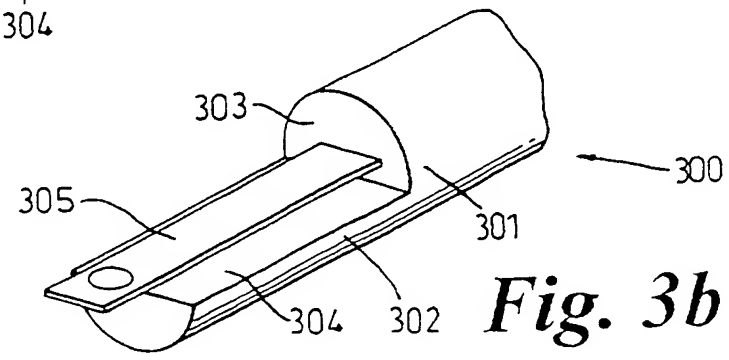

Fig. 3b

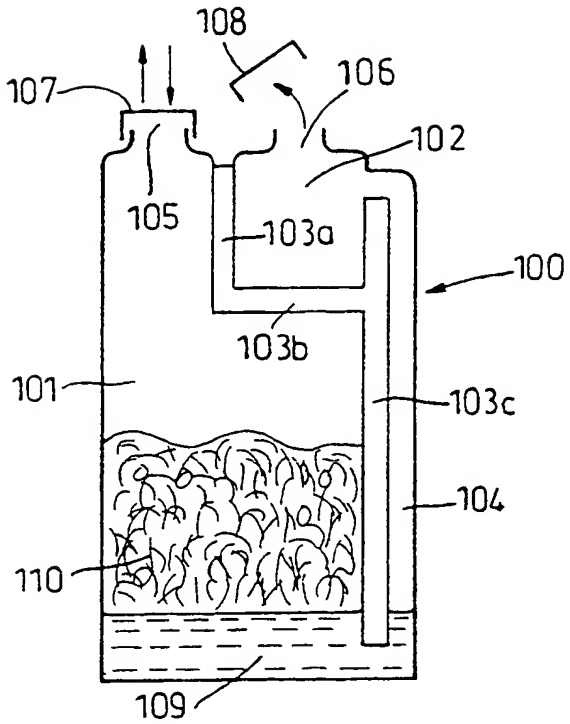

Fig. 4

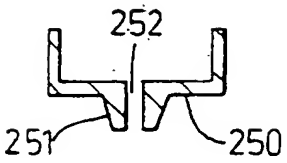

Fig. 5a

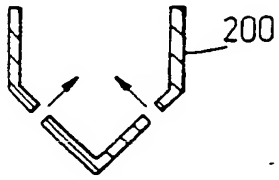

Fig. 5b

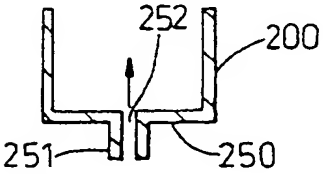

Fig. 5c

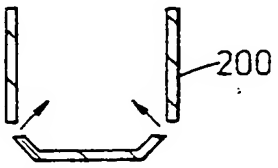

Fig. 5d

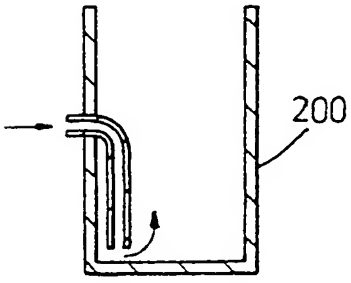

Fig. 5e

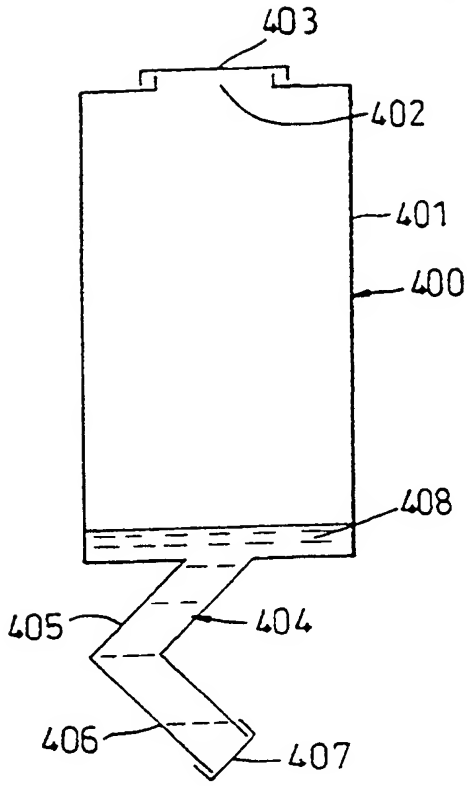

Fig. 6

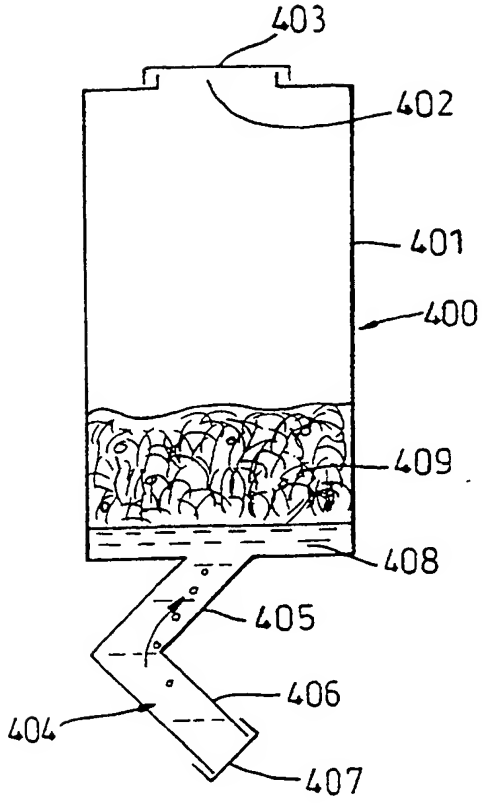

Fig. 7

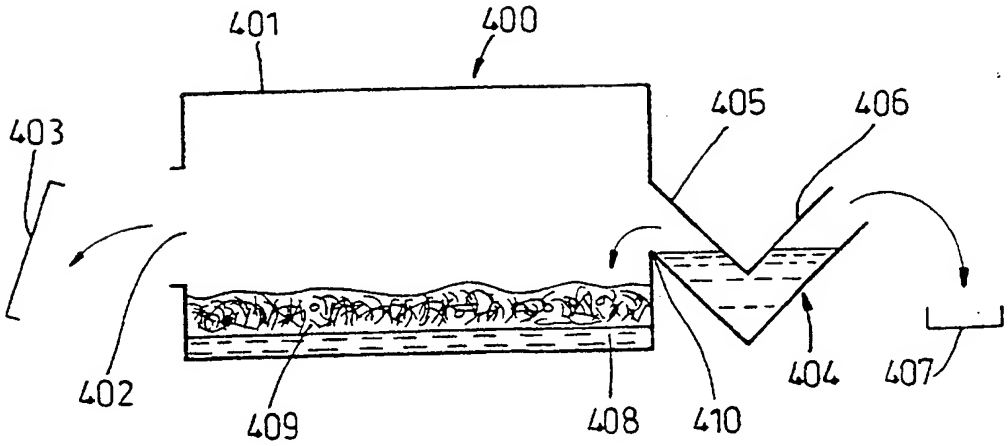

Fig. 8

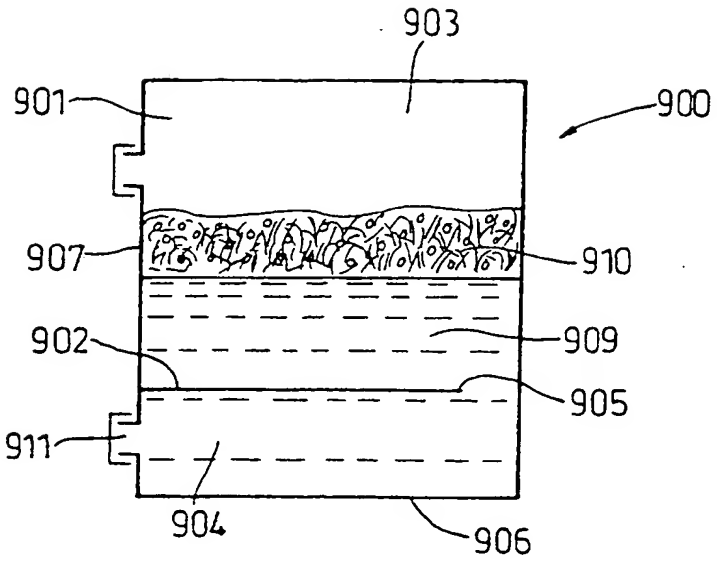
903
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Fig. 9

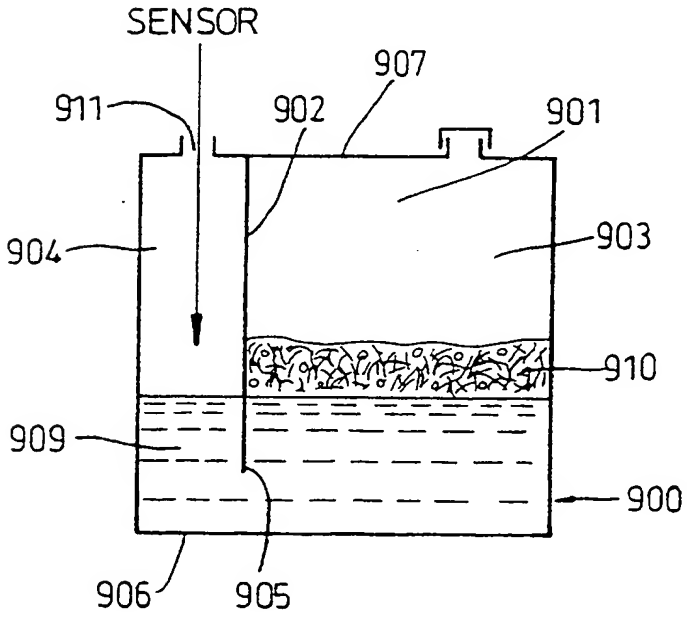
SENSOR
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Fig. 10

ANALYSIS OF LIQUID SAMPLES

The present invention relates to the analysis of liquid media to determine the presence, absence or concentration of a species of interest. The species of interest may be an element or molecule or other chemical species and may include species of biological or industrial origin. The invention relates in particular to methods and apparatus for carrying out such analyses and is especially applicable to point-of-sampling testing.

In many situations where analysis of a liquid (or solid) medium has been required it has been necessary to take a sample of the medium and to forward the sample to a specialised laboratory for analysis. This is disadvantageous in terms of cost (for example because highly trained technicians and expensive instrumentation are required to perform the analysis) and because of the time delay before the results of the analysis are obtained. Thus, for example, in many manufacturing processes results from the analysis of a sample are required immediately in order to check, and if necessary adjust, the process parameters.

Ideally, in order for analysis at the point-of-sampling to be successful, accurate results must be obtainable with equipment which is as simple and robust as possible, capable of carrying out repeated analyses and which requires the minimum level of skill and input from the operator. The present invention seeks to obviate or reduce the above mentioned disadvantages.

The analysis procedures and apparatus of the invention are applicable to a wide variety of species, but one particular use relates to the determination of the alcohol content of an alcoholic beverage - either as a finished product or during the production process - using an electrochemical sensor device.

It is known that the alcohol content of alcoholic beverages (e.g. beer and wine) may be determined by electrochemical sensor devices, e.g. enzyme based amperometric sensors, which are immersed in the beverage for the purpose of effecting the measurement. There are however problems associated with such measurements. For example, the sensor may require a dissolved oxygen content (in the liquid sample being analysed) greater than that normally present in an alcoholic beverage. In this respect, it is relevant to note that beer and wine have a dissolved oxygen content of only about 10% of potential saturated content. Furthermore, alcoholic beverages such as beer and sparkling wine (e.g. champagne) contain dissolved carbon dioxide which can cause problems when it forms bubbles on the working surface of the sensor immersed in the liquid resulting in an incorrect measurement. An additional problem is that carbon dioxide may generate a froth which may interfere with measurements requiring passage of a sensor through the froth before it is immersed in the underlying liquid.

The apparatus and procedures of the present invention provide for improved sample preparation which, in

particular, overcome the above disadvantages.

According to a first aspect of the invention there is provided a method of analysing a liquid sample to determine a species of interest present or potentially present therein, the method including the steps of:

providing a sampling vessel having a main sample chamber containing the liquid to be analysed, a sample analysis region having an openable and closable aperture and a sample flow path between the main chamber and the sample analysis region;

transferring at least a portion of the liquid to be analysed from the main chamber to the sample analysis region via the flow path;

providing a sensor device including a sensor and, before or after said transfer of liquid to the sample analysis region, inserting the sensor device into the sample analysis region through the said openable and closable aperture; and

using the sensor device to make a measurement to determine the species of interest.

Preferably, the main chamber also has an openable and closable aperture through which the liquid sample may be introduced into the main chamber.

The determination to be carried out by the method of the invention may be to determine the presence or absence (or

at least absence above a certain concentration or amount) of the species of interest or the actual concentration or amount of the species.

The vessel is preferably such that it allows for the transfer of a predetermined volume of prepared sample from the main sample chamber to the sample analysis region.

It is an advantage of the invention that the main chamber of the sampling vessel may be used for a sample preparation step to yield a liquid sample which is in a particularly suitable condition for effecting the measurement using the sensor device. The sample preparation step may be a physical or chemical process carried out on a "precursor" of the liquid sample to be determined by the sensor device in the sample analysis region of the sampling vessel.

Thus, by way of example of a physical sample preparation step, the method of the invention may be effected by introducing into the main chamber (as the aforesaid "precursor") a liquid which is then subjected to a sample preparation step involving an exchange of gas between the liquid and its surroundings. The vessel may be such that for liquid (e.g. beer or sparkling wine) generating a froth during the sample preparation step a major proportion of the froth remains in the main sample chamber.

This exchange may for example be for the purpose of

increasing the dissolved oxygen content of the liquid and/or (in the case of a liquid containing dissolved CO_2) to reduce the dissolved carbon dioxide content. The sample preparation step may for example involve shaking of the vessel or spraying of the liquid in a manner which effects the desired exchange of gas.

A further example of a physical sample preparation step is a mixing (e.g. by agitation or swirling of the vessel) of a liquid (the aforesaid "precursor") introduced into the main chamber. Thus, for example, the squeezed juice from all segments of a citrus fruit (e.g. an orange) may be introduced into the main chamber and the vessel swirled around to ensure thorough mixing of the juice to ensure uniform concentration throughout the juice prior to a portion thereof being provided (*via* the flow path) to the sample analysis region for determination of the compound of interest by the sensor device.

Various chemical sample preparation steps are also possible. One example, involves introducing a "precursor" liquid into the main chamber and adding thereto solid or liquid reagents which react with the "precursor" liquid to generate the liquid sample to be provided in the sample analysis region for determination using the sensor device. The reagents may for example be of a chemical (organic or inorganic) or biological nature, e.g. an enzyme.

A further possibility of a chemical sample preparation step involves an extraction procedure effected in the

main chamber using a "precursor" liquid and an immiscible extraction phase into which the compound of interest (if present in the "precursor") is extracted by partitioning. In this case, it is the extraction phase which provides the liquid sample for transfer to the sample analysis region for determination by the sensor device. This procedure is particularly useful for cases where the "precursor" liquid contains an interferent of the detection process, the interferent remaining in the extracted "precursor" liquid. It is of course also possible to envisage extraction of the interferent from the "precursor" liquid and transfer of the latter (extracted) liquid to the sample analysis region.

A further possibility is that, by using appropriate volumes, the extraction may function as a concentration step.

A still further possibility in accordance with the invention is for the "precursor" to be a solid or gas which is introduced into the main chamber and subjected to a chemical treatment to generate a liquid sample (potentially containing the compound of interest) for transfer to the sample analysis region.

In preferred embodiments of the invention, the vessel is in the form of a bottle in which internal walls define a minor chamber which forms the sample analysis region as an upper region of the bottle and further define a passageway for providing the flow path to provide the communication between a lower region of the main chamber

and an upper region of the minor chamber, the apertures of the main and minor chambers each being located at the top of the bottle. A bottle of this type is preferably "squeezable" to allow for the sample liquid to be analysed to be provided in the main (sample preparation) chamber and for the bottle to be squeezed to transfer a portion of the liquid sample to the minor (sample analysis) chamber. Such a bottle may, for example, be of the type disclosed in EP-A-0 010 965 (Bettix).

Alternatively, the sampling vessel may comprise a main chamber provided with a V-shaped tubular arm defining the sample analysis chamber.

The sensor device used for effecting the measurement may for example be an electrochemical sensor, e.g. of the type incorporating an enzyme electrode. In preferred embodiments of the invention, the sensor is an enzyme based amperometric sensor which may, for example, be in planar or needle-like form. The invention does however extend to the use of non-enzymic and non-electrochemical sensors, e.g. colorimetric "dipsticks".

The method of the invention preferably uses a sensor device on or in which the sensor is mounted and which is such that it (the sensor device) may be supported relative to the sample analysis region so that the sensor extends by a predetermined distance into that region to provide for a known depth of immersion of the sensor in the liquid sample to be analysed. The sensor device is preferably such that a sensor is removably mounted

thereon. This allows the use of disposable sensors. The sensor device may, for example, comprise an enlarged head portion connected to an elongate finger along which the sensor extends. The sensor device may for example incorporate a plurality of sensors for determining different analytes of interest in the liquid sample. The sensor device preferably also comprises a temperature sensor for immersion in the liquid whereby compensation may be made for the temperature of the sample.

A second aspect of the invention provides a component which ensures that the sensor is removably located in a predetermined location in the sample chamber. In this way, it is possible to eliminate any variation in the depth of insertion of the sensor in the liquid sample, which variations could affect the accuracy of the analysis. This component also serves to protect the sensor from mechanical damage, in use. Accordingly, this aspect of the invention provides a support component for supporting a sensor device incorporating a sensor such that the sensor is operatively maintained in a predetermined relation to a vessel for containing a liquid sample, the support component comprising a generally tubular body portion, at least one orifice, formed in the body portion, for the ingress of liquid, first mounting means operative to co-operate with the vessel so that the body portion operatively lies in a predetermined position at least partially within the vessel and second mounting means operative to co-operate with the sensor device so that the sensor lies in a predetermined position within the body portion.

In a preferred embodiment of this second aspect, the first mounting means comprises a laterally extending flange operative to rest on a neck of the container.

In a particularly preferred embodiment of this aspect of the invention, ingress of sample liquid to the interior of the support component is provided by a relatively small orifice. Thus, in this embodiment the support component has, opposite to its open end, a planar end closure part generally perpendicular to the longitudinal axis of the tubular body portion, and an inlet tube mounted on said closure part, which inlet tube is in communication with the tubular body by means of said small orifice formed in said closure part, and said inlet tube having an internal diameter substantially equal to the diameter of said small orifice. In particular constructions, the tubular body portion, the closure part and the inlet tube may be formed separately or integrally.

In another preferred embodiment, the body portion is of generally circular cross section with a conical tip, in which tip an orifice is formed.

Such a support component is useful for analysis procedures in which froth on the prepared liquid sample enters the sampling region. The provision of the small cross-section orifice allows ingress of only liquid (and not froth) to the interior of the support component whereby the sensor device is immersed in an "un-frothed"

sample of the liquid for the purposes of effecting the measurement.

The invention also provides, in further aspects, apparatus used in carrying out the method as described above. Therefore, according to a third aspect of the present invention there is provided apparatus for analysis of liquid samples comprising:

a sampling vessel having a main chamber forming a sample preparation region and having an openable and closable aperture through which liquid may be introduced into the main chamber and a sample analysis region separate from and in fluid communication with the main chamber and having an openable and closable aperture through which a sensor device may be inserted for immersion in liquid in the sample analysis region, and

a support component for supporting the sensor device to a predetermined depth in the sample analysis region.

In a fourth aspect of the invention, there is provided apparatus for analysing liquid samples comprising:

a sampling vessel having a sample analysis region, said region having an openable and closable aperture;

a sensor device for immersion into the liquid sample, through the aperture; and

a support component mountable over the said aperture for supporting the sensor device to a predetermined depth in the sample analysis region.

In one preferred embodiment of this aspect of the invention, the sensor device comprises an electrochemical sensor comprising a substrate having one or more electrodes formed thereon, and a sensor mounting component operatively retaining the sensor and including one or more contacts for electrical connection with the respective one or more electrodes, said sensor mounting component being operatively supported by the said support component.

In this aspect, preferably the apparatus further comprises a measuring instrument operatively electrically connected to the sensor device and operative to analyse electrical signals from the sensor device and to provide an output representative of the concentration of a desired species in the liquid samples.

In order to allow efficient and stable interaction with the support component, and for ease of handling, preferably the sensor mounting component comprises an enlarged head portion connected to an elongate finger along which the sensor extends.

Desirably, the sensor device also incorporates a temperature sensor so that the analysis can compensate for temperature variations.

A fifth embodiment of the invention provides apparatus for determining the concentration of a species of interest in a liquid sample, the apparatus comprising:

an electrochemical sensor comprising a substrate having one or more electrodes formed thereon;

a sensor mounting component operatively retaining the sensor and including one or more contacts for electrical connection with the respective one or more electrodes;

a measuring instrument operatively electrically connected to the sensor via the sensor mounting component and operative to analyse electrical signals produced by the sensor and to provide an output representative of the concentration of the species being determined; and

a sampling vessel for containing the liquid sample, having a sample analysis region, said region having an openable and closable aperture for insertion of the sensor into the said region.

It is particularly preferred in this aspect of the invention that the apparatus further comprises a support component mountable over the said openable and closable aperture for supporting the sensor mounting component whereby the sensor is disposed in the sample analysis area to a predetermined depth.

In a sixth aspect of the invention, there is provided a configuration of the apparatus of the invention

especially suitable for point-of-sampling testing, most particularly where testing is required "in the field" away from industrial premises. This aspect provides apparatus for point-of-sampling analysis of liquid samples, the apparatus comprising the following component parts:

a container for containing the liquid sample, having a sample analysis region, said region having an openable and closable aperture;

a plurality of electrochemical sensors, each comprising a substrate having one or more electrodes formed thereon;

a sensor mounting component operative to retain a sensor and including one or more contacts for electrical connection with the respective one or more electrodes;

a measuring instrument operatively electrically connectable to a sensor when said sensor is retained in said sensor mounting component and operative to analyse electrical signals produced by the sensor and to provide an output representative of the concentration of a desired species in the liquid samples; and

a case for storing and/or transporting the above mentioned component parts.

It is particularly preferred in this aspect of the invention that the apparatus further comprises a support component operatively mountable over the openable and

closable aperture for supporting the sensor mounting component whereby the sensor is disposed in the sample analysis region to a predetermined depth.

In preferred embodiments of the fifth and sixth aspects of the invention the sensor mounting component comprises an enlarged head portion connected to an elongate finger along which the sensor extends.

Also in these embodiments the sensor device preferably incorporates a temperature sensor.

The second to sixth aspects of the invention also encompass embodiments wherein the vessel is in the form of a squeezable bottle in which the internal walls define a minor chamber which forms the sample analysis region as an upper region of the bottle and further define a flow path for providing communication between a lower region of the main chamber and an upper region of the minor chamber, the apertures of the main and minor chamber each being located at the top of the bottle.

Alternatively, the sample vessel may comprise a main chamber provided with a V-shaped tabular arm defining the sample analysis region.

In a seventh aspect of the invention, there is provided apparatus for use in analysing a liquid sample to determine a species present or potentially present therein, the apparatus comprising a sampling vessel including a top wall, a baffle dividing the vessel into a

main region and a sample analysis region, and, an openable and closeable aperture formed in the top wall in the sample analysis region, said baffle extending in a first direction away from the top wall for a distance less than the internal dimension of the vessel such that the baffle has a free end distant from the openable and closeable aperture and extending in a second direction, generally perpendicular to the first direction, across the entire width of the vessel, whereby a flow path between the main region and the sample analysis region exists only around the free end of the baffle. Preferably the apparatus further comprises a second openable and closeable aperture formed in the top wall in the main region.

In a related eighth aspect of the invention, there is provided a method of analysing a liquid sample to determine a species present or potentially present therein, the method comprising:

providing apparatus as defined in the seventh aspect of the invention;

filling the vessel with a liquid sample through an openable and closeable aperture to a level whereby, when the vessel is oriented in a first orientation such that the top wall is substantially vertical and the baffle is in a lower part of the vessel, the liquid sample level is higher than the baffle, and closing the vessel;

rotating the vessel from said first orientation though

approximately 90° so that the top wall is approximately horizontal;

opening the aperture in the sample analysis region;

providing a sensor device including a sensor and inserting the sensor device into the sample analysis region through the openable and closeable aperture; and

using the sensor device to make a measurement to determine the species of interest.

In particularly preferred embodiments, the method further includes a sample preparation step after filling of the vessel. These sample preparation steps may be any of those outlined herein.

Preferably the sample preparation step includes the step of shaking the vessel when in its first orientation. This shaking may be to effect oxygenation and/or degassing of the sample. Such shaking will often generate a foam and the above-noted baffle is effective in preventing the foam from being present to a significant extent in the sample analysis region of the apparatus.

The method and apparatus of the present invention are particularly useful for determining the alcohol content of an alcoholic beverage since the method of the invention allows easy and efficient sample preparation to increase dissolved oxygen content and/or reduce dissolved

carbon dioxide content thereby appropriately conditioning the sample for measurement with the sensor device. The measurement of alcohol content may, for example, be for the purpose of monitoring fermentation (to decide whether fermentation is complete or whether yeast and/or sugar should be added) or for measuring alcohol content prior to barrelling/bottling for Excise duty purposes.

The invention will be further described by way of Example only with reference to the accompanying drawings in which:

Fig 1 illustrates a sampling vessel;

Fig 2 illustrates an assembly of part of the vessel shown in Fig 1, a support component, and a sensor device;

Figs 3a and 3b are a detailed views of sensor devices;

Fig 4 illustrates a step in a sample preparation;

Figs 5a to 5e illustrate various embodiments of support component;

Figs 6 - 8 illustrate sample preparation in accordance with a one embodiment of the invention; and

Figs 9 and 10 illustrate sample preparation in accordance with the seventh and eighth aspects of the invention.

The sampling procedure to be described below utilises a sampling vessel 100 (see Fig 1), a support component 200 (see Fig 2) and a sensor device 300 incorporating a sensor 305 (see Fig 3).

The sampling vessel 100 illustrated in Fig 1 is in the form of a bottle comprising a major chamber 101 and a minor chamber 102 forming the sample analysis region. The minor chamber 102 is defined by internal walls 103a-c of the vessel. As illustrated in the drawing, chamber 102 is at an upper region of the vessel 100 and is in communication with chamber 101 via a flow path in the form of a passageway 104 defined by interior wall 103c. Passageway 104 extends between a lower liquid transfer port 104a (at a lower region of the major chamber 101) and an upper liquid transfer port 104b (at an upper region of the sample analysis chamber 102). Each of chambers 101 and 102 has a respective upper aperture 105 and 106 provided with a removable cap 107 or 108.

Vessel 100 is formed of a pliable plastics material permitting the transfer (by squeezing of the vessel) of liquid from main chamber 101 to sampling chamber 102 as described more fully below.

The vessel 100 may, for example, be of the type disclosed in EP-A-0 010 965 (Bettix).

Reference is now made to Fig 2 illustrating the support component 200 which will be seen to comprise a generally

cylindrical body 201 with an outer diameter less than the inner diameter of aperture 106. The body 201 may alternatively be of any suitable cross-sectional shape, such as square, rectangular or hexagonal. In one variation, as illustrated in Figure 2, at its lower end the body 201 has a downwardly tapering conical tip 202 with an apical aperture 203. Other possible constructions are shown in Figure 5, of which those of Figures 5a and 5c are preferred. Towards its upper end, the body 201 is provided with an external annular flange 204 with a depending skirt 205. It will be appreciated from Fig 2 that the support component 200 is dimensioned to allow the body 201 to be inserted through the opening 106 such that the support component 200 is supported by virtue of the flange 204 resting on the lip of aperture 106 and with its tip below the level of part 104b but above the base of chamber 102.

It will be seen from Fig 2 that the support component 200 (supported on the opening 106 as described) is able to locate in position a sensor device 300 shown in more detail in Fig 3 to which reference is now made. Sensor device 300 comprises an enlarged head portion 301 connected to an elongate finger 302 which is partially "cut-away" whereby the finger includes a shoulder 303 and a longitudinally extending flat section 304. An electrochemical sensor 305 (e.g. an enzyme based amperometric sensor) is removably connectable through a contact arrangement 306 located in the shoulder 303. A temperature sensor 307 is provided at the free end of finger 302 as shown. As illustrated in Fig 3a, the free

end of the finger 302 extends beyond the end of the sensor 305. This need not necessarily be so and as illustrated in Fig 3b the finger 302 may be shorter than the sensor 305, provided that the sensor is adequately supported. Wires (not shown) for connecting the electrochemical sensor 305 and temperature sensor 307 to the necessary electronic measuring and control apparatus extend from the contacts 306 and temperature sensor 307 through the finger 303 and head 301.

As will be appreciated from Fig 2, the sensor device 300 is such that it may be supported by means of its head 301 in the support component 200 so that the sensing area of the liquid electrochemical sensor 305 is fully immersed in the liquid.

The electrochemical sensor 305 may for example be an enzyme based amperometric sensor capable of measuring the concentration of alcohol (or other species of interest) present in the liquid. The characteristics of such alcohol sensors are such that a minimum dissolved oxygen content is generally required in the liquid analyte sample and measurements are adversely influenced by the formation of gas bubbles on the sensor surface. Alternatively the sensor 305 may be for determining a different analyte or may incorporate several sensor areas on a single element for determining different analytes.

The manner in which the components thus far described with reference to Figs 1-3 are used for effecting a measurement on a liquid sample will now be described.

Initially, liquid 109 to be analysed (e.g. an alcoholic beverage such as beer or wine) is introduced into the main chamber 101 of the sampling vessel 100 to a level which may be (but is not necessarily) above the lower liquid transfer port 104a and the caps 107 and 108 are located in position. The volume of liquid to be added will be dependent on the type of sample. For example, if the chamber 101 has a volume of 500ml then it would be appropriate to use 100ml of wine. Alternatively, 25ml of beer would be appropriate for a 500ml chamber. In the case of relatively small volumes of liquid it is alternatively possible to introduce the liquid firstly into sample analysis chamber 102 and then tilt the bottle 100 so that the liquid is transferred into chamber 101. This procedure has the advantage (for small volumes of liquid) in that the small chamber 102 may have a gradation mark which more accurately represents the relatively small volume of liquid than would a gradation mark (for the sample volume) on the chamber 101. In another variation, one of the closures 106,108 may be used to measure an appropriate sample volume, or some other specific container may be provided for this purpose.

Vessel 100 is then shaken (e.g. 10-30 vigorous shakes or thirty seconds continuous shaking will generally be appropriate) which results in an exchange of gas between the liquid and its surroundings with a two-fold effect. Firstly, carbon dioxide is released from the liquid possibly generating a froth 110 (see Fig 4). Secondly,

the dissolved oxygen content of the liquid is increased thereby "conditioning" the liquid for measurement with the sensor which (as mentioned above) may require a minimum dissolved oxygen content. A mesh or baffles may be disposed in the interior of the main chamber 101 to increase the efficacy of the shaking. In a variation of the procedure, an anti-foam agent may be added to the sample in the main chamber 101 provided that the anti-foam agent does not interfere with the analysis.

Caps 107 and 108 are then removed (in that order) prior to cap 107 being replaced and tightened. This procedure ensures that any excess gas build-up within the vessel is released without the liquid entering the sample analysis chamber 102. This pressure release step may additionally be performed during a pause in the shaking. Alternatively, a pressure release valve may be provided in the main (and minor) chambers. In another variation, the vessel may include at least one small hole at an upper part of the side walls for the release of excess pressure.

After the pressure release, the main chamber 101 is squeezed so that the sample liquid travels upwardly through passageway 104 to fill the sample analysis chamber 101. (In the case where the chamber 101 contains a relatively low volume of liquid it may be necessary to tilt the bottle to ensure that port 104a is covered). A valve or tap me be provided at port 104a to prevent transfer of the liquid sample into passageway 104 until desired. The compression of main chamber 101 is then

released permitting a volume of sample to remain in chamber 102 (upto the level of part 104b with the vessel 100 vertical, or lower in some cases) whilst excess is sucked back into the main chamber 101. Since the liquid level in main chamber 101 is often above port 104a, most of the froth remains in main chamber 101 although a portion may enter the sample analysis chamber 102. A bubble filter of bubble trap may be incorporated in the passageway 104 if desired, to reduce the possibility of transmission of foam into the chamber 102. After this point, the aperture 105 may be left open or closed.

In the next stage of the procedure, support component 200 is inserted into chamber 102 so that its conical tip 202 (or other leading end construction, such as those of Figure 5) is below the level of the liquid 109 therein. The shape of support component 200 ensures that it "parts" the froth as it passes therethrough and as a result the lower region of body 201 and the tip 202 contain an "un-frothed" sample of liquid. Subsequently, the sensor device 300 is inserted into the support component 200 so that the lower end of the sensor 305 is immersed in the liquid 109. The positioning of the sensor device 300 in the support component 200 ensures a predetermined immersion depth for the sensor 305. Since many sensors are susceptible to excess liquid causing problems of corrosion, contamination or electrical short circuits, the use of the support component 200 overcomes these problems.

Although advantageous, the use of the support component

200 is not essential. Thus, the relative constructions of the sensor device 300 and the minor chamber 102 may be such as to provide a predetermined depth of immersion of the sensor 305. In one possible variation, the sensor may have a needle like construction and the closure 108 may be in the form of a rubber septum which is pierced by the sensor. In this construction, additional ventilation of the minor chamber 102 may be required.

It should at this point be appreciated that there are clearances between the outer surface of body 201 (of the support component 200) and the inner surface of aperture 106 and also between the inner surface of body 201 and the sensing head 300. These clearances avoid problems with "piston effects" and capillary filing of narrow gaps. Such problems could otherwise arise if the components are wet from rinsing or from a previous measurement. In a modification (not illustrated) spacers may be provided on the lower surface of flange 204 to avoid a seal being formed with the annular rim defining the aperture 106. Thus a clear air space continuous from the atmosphere to the interior of chamber 102 and from the atmosphere to the interior of the support component 200 is defined such that the clearances are not liable to be filled by capillary action or stray droplets of liquid. In a further modification (not illustrated) the clearances may be achieved by providing (additionally to or alternatively to the annular flange 204 and skirt 205) the body 201 with circumferentially spaced, longitudinally extending fins provided on the exterior surface of the body 201 whereby the support component 200

is a push fit within the aperture 106. Furthermore, the exterior surface of the cylindrical portion of the elongate finger 302 (of the sensing arrangement 300) may also be provided with circumferentially spaced, longitudinally extending fins whereby the cylindrical portion 302 is a push fit in the support component 200.

A measurement may now be made of the alcohol (or other analyte) content of the beverage, It will be appreciated from the forgoing description that the liquid 109 in the chamber 102 is of appropriate dissolved oxygen content to permit the sensor 305 to function correctly. Moreover, the liquid 109 in the chamber 102 is of reduced carbon dioxide content (as compared to the original liquid sample) so that problems associated with bubble formation on the sensor immersed in the liquid are minimised or avoided completely. Furthermore, there is no interference resulting from plunging the sensor through a froth to the underlying liquid.

In a modification of the above procedure, the support component 200 may be inserted into, and supported by, the aperture 106 prior to squeezing the bottle to introduce the liquid into the sampling chamber 102. In further modifications of the technique described, the lower end of the support component 200 may have any of the alternative configurations illustrated in Fig 5. All of these are characterised by the feature that they include one or more restricted openings permitting liquid to enter the support component but preventing the ingress of froth. In the preferred constructions of Figures 5a and

5c, the leading (lower) end of the component 200 has a generally planar end closure part 250 with an inlet tube 251. The inlet tube 251 communicates with the interior of the component 200 by means of an orifice 252 in the end closure part 250.

In order to facilitate cleaning of the vessel 100 after use, further apertures may be provided to allow a through flow of cleaning fluid (eg water).

Reference is now made to Figs 6 - 8 which illustrate a further embodiment of the invention. Referring to Fig 6, there is illustrated a sampling vessel 400 having a generally cylindrical body 401 provided in one end face with an aperture 402 closed by a removable cap 403. At its end opposite to opening 402, the body 401 is provided with a V-shaped tubular arm 404 formed by limbs 405 and 406. Limb 405 communicates with the interior of body 401 and the end of limb 406 is provided with a removable cap 407.

For use in sample preparation, the vessel 400 is positioned with opening 402 uppermost (as illustrated in Fig 6). With cap 407 in position, liquid sample 408 is introduced into the vessel so as to enter and fill the V-shaped tubular arm 404 such that there may also be liquid in the base of body 401. Vessel 400 is now shaken as previously. Gas bubbles rise from the tubular arm 404 (Fig 7) so that any froth 409 is mostly within the body 401 and only "un-frothed" liquid remains in the distal end of the tubular arm 406. Careful rotation of vessel

400 so that its longitudinal axis becomes horizontal (Fig 8) ensures that substantially all of the froth remains in the (now horizontal) body 401 and a defined volume of liquid is in the tubular arm 404. Cap 403 and then 407 may now be removed and a sensor inserted so as to effect a measurement as previously described.

The depth of immersion of the sensor is controlled by the level of liquid in the arm 406. This may in turn be controlled by ensuring that, with the body 101 horizontal, the level of the liquid is below the lip 410 (at the junction between the body 401 and the side arm 405). On opening cap 403 and then cap 407 the level of the liquid in the side arm 404 will drop to that defined by lip 410.

The shape and dimensions of the apparatus illustrated in Figs 6 - 8 are not critical and the V-shaped arm could be replaced by a U-shaped arm or a complex series of baffles. The key point is the separation of froth by a partition - in the illustrated embodiment by the upper side of the "V" at the junction of arms 405 and 406.

Referring now to Figures 9 and 10, in which there is illustrated an alternative sample preparation vessel in accordance with the seventh and eighth aspects of the invention. This vessel may be used in combination with the sensor device and sensor support component in the same manner as for the other aspects of the invention, and these will not be described further.

The vessel 900 of Figures 9 and 10 comprises a single chamber 901 which is divided by a baffle 902 into a main region 903 and a sample analysis region 904. The baffle 902 extends across the full width of the vessel 900 but its free end 905 is spaced apart from the base 906 of the vessel 900. The baffle 902 depends from the top wall 907 of the vessel 900. The top wall 907 includes and openable and closeable aperture 911 in the sample analysis region 904 and an optional openable and closeable aperture in the main region 903.

In use, the vessel 900 is filled with liquid sample 909 until, with the vessel 900 in the orientation illustrated in Figure 9, the baffle 902 is submerged. After filling the sample preparation steps (which may be any of those previously mentioned) may be carried out. The vessel 900 is closed at an appropriate point in these steps. Preferably the preparation step is a shaking step for degassing and/or oxygenating the sample. In this case, after the container is closed, it is shaken in the orientation shown in Figure 9. This shaking will normally generate an undesirable foam 910, which could interfere with the accuracy of measurements taken with the sensor (see below). Thus, in order to ensure that there is no foam 910, or a minimum of foam 910 in the sample analysis region 904, the vessel 900 is carefully rotated through about 90° in (in the example illustrated) a clockwise direction, so that the vessel 900 adopts the orientation shown in Figure 10. In this way, the baffle 902 prevents all, or the majority, of the foam 910 from passing into the sample analysis region 904.

The aperture 911 in the sample analysis region 904 may then be opened and a sensor device including a sensor inserted through the aperture 911 so that the sensor enters the liquid sample. A measurement of the species to be determined may then be made with the sensor device.

It will be appreciated from the foregoing description that the illustrated embodiments provide a simple, quick and inexpensive means of sample preparation and analysis.

CLAIMS

1. A method of analysing a liquid sample to determine a species of interest present or potentially present therein, the method including the steps of:

providing a sampling vessel having a main sample chamber containing the liquid to be analysed, a sample analysis region having an openable and closable aperture, and having a sample flow path between the main chamber and the sample analysis region;

transferring at least a portion of the liquid to be analysed from the main chamber to the sample analysis region via the flow path;

providing a sensor device including a sensor and, before or after said transfer of liquid to the sample analysis region, inserting the sensor device into the sample analysis region through the said openable and closable aperture; and

using the sensor device to make a measurement to determine the species of interest.

2. A method as claimed in claim 1 wherein the main chamber has an openable and closable aperture through which the liquid may be introduced into the main chamber.

3. A method as claimed in claim 2 wherein the vessel is in the form of a bottle in which internal walls define a minor chamber which forms the sample

analysis region as an upper region of the bottle and further define a passageway for providing the flow path to provide the communication between a lower region of the main chamber and an upper region of the minor chamber, the apertures of the main and minor chambers each being located at the top of the bottle.

4. A method as claimed in claim 3 wherein the bottle is "squeezable" to provide for transfer of liquid sample from the main chamber to the minor chamber.

5. A method as claimed in claim 1 or 2 wherein the sampling vessel comprises a main chamber provided with a V-shaped tubular arm defining the sample analysis region.

6. A method as claimed in any one of claims 1 to 5 wherein a precursor of the liquid sample is first introduced into the main chamber and subjected to a sample preparation step to provide the liquid sample to be analysed.

7. A method as claimed in claim 6 wherein the sample preparation step is a physical step.

8. A method as claimed in claim 7 wherein the sample preparation step comprises shaking the vessel to provide for an exchange of gas between the liquid and its surroundings.

9. A method as claimed in claim 8 wherein the sample preparation step results in generation of a froth and, on transfer of the liquid sample analysis

region, a major proportion of the froth remains in the main chamber.

10. A method as claimed in claim 6 wherein the sample preparation step is a chemical step.

11. A method as claimed in claim 10 wherein solid or liquid reagents are added to the precursor liquid in the main chamber to generate the liquid sample to be provided in the sample analysis region.

12. A method as claimed in claim 11 wherein the reagent is a biological reagent.

13. A method as claimed in claim 12 wherein the reagent is an enzyme.

14. A method as claimed in claim 6 wherein the sample preparation step involves an extraction of the precursor of the liquid sample.

15. A method as claimed in any one of claims 1 to 14 utilising a sensor device on which the sensor is mounted and which is such that the sensor device may be supported relative to the sample analysis region so that the sensor extends by a predetermined distance into that region to provide for a known depth of immersion of the sensor in the liquid sample to be analysed.

16. A method as claimed in claim 15 wherein the sensor device is such that the sensor is removably mounted thereon.

17. A method as claimed in claim 15 or 16 wherein the sensor device comprises an enlarged head portion connected to an elongate finger along which the sensor extends.

18. A method as claimed in any one claims 15 to 17 wherein the sensor device incorporates a temperature sensor.

19. A method as claimed in any one of claims 15 to 18 wherein a support component is removably mounted in the sample analysis region and the sensor device is supported by the support component.

20. A method as claimed in claim 19 wherein the support component comprises a tubular body having an open end into which the sensor device may be inserted and is enclosed at its other end save for at least one small orifice to permit ingress of liquid but not foam.

21. A method as claimed in claim 20 wherein the support component has, opposite to its open end, a planar end closure part generally perpendicular to the longitudinal axis of the tubular body portion, and an inlet tube mounted on said closure part, which inlet tube is in communication with the tubular body by means of said small orifice formed in said closure part, and said inlet tube having an internal diameter substantially equal to the diameter of said small orifice.

22. A method as claimed in any one of claims 1 to 21 wherein the sensor is an electrochemical sensor.

23. A method as claimed in claim 22 wherein the electrochemical sensor incorporates an enzyme electrode.

24. A method as claimed in claim 23 wherein the electrochemical sensor is an enzyme based amperometric sensor.

25. A method as claimed in any one of claims 1 to 21 wherein the sensor device is a non-enzymic sensor.

26. A method as claimed in claim 24 wherein the sensor is a colourimetric sensor.

27. A method as claimed in any one of claims 1 to 26 for measurement of alcohol content.

28. Apparatus for analysis of liquid samples comprising:

a sampling vessel having a main chamber forming a sample preparation region and having an openable and closable aperture through which liquid may be introduced into the main chamber, and a sample analysis region separate from and in fluid communication with the main chamber and having an openable and closable aperture through which a sensor device may be inserted for immersion in liquid in the sample analysis region, and

a support component for supporting the sensor device to a predetermined depth in the sample analysis region.

29. Apparatus for analysing liquid samples comprising:

a sampling vessel having a sample analysis region, said region having an openable and closable aperture

a sensor device for immersion into the liquid sample, through the aperture and

a support component mountable over the said aperture for supporting the sensor device to a predetermined depth in the sample analysis region.

30. Apparatus as claimed in claim 29 wherein the sensor device comprises an electrochemical sensor comprising a substrate having one or more electrodes formed thereon, and a sensor mounting component operatively retaining the sensor and including one or more contacts for electrical connection with the respective one or more electrodes, said sensor mounting component being operatively supported by the said support component

31. Apparatus as claimed in claim 29 or 30 further comprising a measuring instrument operatively electrically connected to the sensor device and operative to analyse electrical signals from the sensor device and to provide an output representative of the concentration of a desired species in the liquid samples.

32. Apparatus as claimed in claim 30 wherein the sensor mounting component comprises an enlarged head portion connected to an elongate finger along which the sensor extends.

33. Apparatus as claimed in any of claims 29 to 32 wherein the sensor device incorporates a temperature sensor.

34. Apparatus for determining the concentration of a species of interest in a liquid sample, the apparatus comprising:

an electrochemical sensor comprising a substrate having one or more electrodes formed thereon;

a sensor mounting component operatively retaining the sensor and including one or more contacts for electrical connection with the respective one or more electrodes;

a measuring instrument operatively electrically connected to the sensor via the sensor mounting component and operative to analyse electrical signals produced by the sensor and to provide an output representative of the concentration of the species being determined; and

a sampling vessel for containing the liquid sample, having a sample analysis region, said region having an openable and closable aperture for insertion of the sensor into the said region.

35. Apparatus as claimed in claim 34 further comprising a support component mountable over the said openable and closable aperture for supporting the sensor mounting component whereby the sensor is disposed in the sample analysis area to a predetermined depth.

36. Apparatus for point-of-sampling analysis of liquid samples, the apparatus comprising the following components parts:

a vessel for containing the liquid sample, having a sample analysis region, said region having an openable and closable aperture;

a plurality of electrochemical sensors, each comprising a substrate having one or more electrodes formed thereon;

a sensor mounting component operative to retain a sensor and including one or more contacts for electrical connection with the respective one or more electrodes;

a measuring instrument operatively electrically connectable to a sensor when said sensor is retained in said sensor mounting component and operative to analyse electrical signals produced by the sensor and to provide an output representative of the concentration of a desired species in the liquid samples; and

a case for storing and/or transporting the above mentioned component parts.

37. Apparatus as claimed in claim 36 further comprising a support component operatively mountable over the openable and closable aperture for supporting the sensor mounting component whereby the sensor is disposed in the sample analysis region to a predetermined depth.

38. Apparatus as claimed in any of claims 34 to 37 wherein the sensor mounting component comprises an enlarged head portion connected to an elongated finger along which the sensor extends.

39. Apparatus as claimed in any of claims 34 to 38 wherein the sensor device incorporates a temperature sensor.

40. Apparatus as claimed in any of claims 28 to 39 wherein the vessel is in the form of a squeezable bottle in which the internal walls define a major chamber and a minor chamber which minor chamber forms the sample analysis region as an upper region of the bottle and which walls further define a flow path for providing communication between a lower region of the main chamber and an upper region of the minor chamber, the apertures of the main and minor chambers each being located at the top of the bottle.

41. Apparatus as claimed in any of claims 28 to 39 wherein the vessel comprises a main chamber provided with a V-shaped tubular arm defining the sample analysis region.

42. A support component for supporting a sensor device incorporating a sensor such that the sensor is operatively maintained in a predetermined relation to a vessel for containing a liquid sample, the support component comprising a generally tubular body portion, at least one orifice, formed in the body portion, for the ingress of liquid, first

mounting means operative to co-operate with the vessel so that the body portion operatively lies in a predetermined position at least partially within the vessel and second mounting means operative to co-operate with the sensor device so that the sensor lies in a predetermined position within the body portion.

43. A support component as claimed in claim 42 wherein the first mounting means comprises a laterally extending flange operative to rest on a neck of the container.

44. A support component as claimed in claim 42 or 43 wherein the body portion is of generally circular cross-section with a conical tip, in which tip an orifice is formed.

45. Apparatus as claimed in any of claims 28, 29 to 33, 35 or 37 or any of claims 38 to 40 when dependant on the above claims wherein the support component is as defined in any of the claims 41 to 43.

46. Apparatus for use in analysing a liquid sample to determine a species present or potentially present therein, the apparatus comprising

a sampling vessel including a top wall, a baffle dividing the vessel into a main region and a sample analysis region, and, an openable and closeable aperture formed in the top wall in the sample analysis region, said baffle extending in a first direction away from the top wall for a distance less than the internal dimension of the vessel such that

the baffle has a free end distant from the openable and closeable aperture and extending in a second direction, generally perpendicular to the first direction, across the entire width of the vessel, whereby a flow path between the main region and the sample analysis region exists only around the free end of the baffle.

47. Apparatus as claimed in claim 46 further comprising a second openable and closeable aperture formed in the top wall in the main region

48. A method of analysing a liquid sample to determine a species present or potentially present therein, the method comprising:

providing apparatus as claimed in claim 46 or 47;

filling the vessel with a liquid sample through an openable and closeable aperture to a level whereby, when the vessel is oriented in a first orientation such that the top wall is substantially vertical and the baffle is in a lower part of the vessel, the liquid sample level is higher than the baffle, and closing the vessel;

rotating the vessel from said first orientation though approximately 90° so that the top wall is approximately horizontal;

opening the aperture in the sample analysis region;

providing a sensor device including a sensor and inserting the sensor device into the sample analysis

region through the openable and closeable aperture; and

using the sensor device to make a measurement to determine the species of interest.

49. A method as claimed in claim 48 further including a sample preparation step after filling of the vessel.

50. A method as claimed in claim 49 wherein the sample preparation step includes the step of shaking the vessel when in its first orientation.

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Claims searched: 1 - 28

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Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.S): G1B (BCE, BCF, BCK); B1X (X8)

Int Cl (Ed.7): G01N 1/00; B01L 3/00, 11/00; G01F 11/28

Other:

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
A	WO 96/37177 A2	(NBA) e.g. see Figures 1 & 2; Page 4 lines 17 -26; Page 13 lines 4 etc.	1 & 28
A	GB 2038779 A	(BETTIX) (equivalent to EP 0010965 A - mentioned in the application) *see whole document*	28
A	US 4418843	(BETTIX) e.g. see Figures 1 - 4.	28

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
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